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CHARACTERIZATION OF SURFACE-MODIFIED PET FILMS FROM INDUSTRY

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ฟิล์มพอลิเอทิลีนเทเรฟทาเลต จากอุตสาหกรรมการบรรจุแบบยืดหยุ่น ที่ผ่านการดัดแปรโดยโคโรนาภายใต้สภาวะอากาศปรกติ ความเร็วในการผลิต ที่ 410 210 และ 150 เมตรต่อนาที ใช้พลังงานไฟฟ้า ที่ 6.7 และ 9.0 กิโลวัตต์ การดัดแปรโดยพลาสมาภายใต้สภาวะสุญญากาศ โดยการเติมแก๊ส ออกซิเจนและอาร์กอน ความเร็วในการผลิตที่ 600 เมตรต่อนาที ใช้พลังงานไฟฟ้า ที่ 4.0 กิโลวัตต์ และการดัดแปรโดยสารเคมี โดยการเคลือบอนุพันธ์ของ อะมิโน เรซิ่น อุปกรณ์ที่ใช้ในการศึกษาครั้งนี้ คือ เอทีอาร์เอฟทีไออาร์สเปกโทรสโคปี และรามานสเปกโทรสโกปี ในการวิเคราะห์โครงสร้างทางเคมีหรือหมู่ฟังก์ชัน เช่น เอสเตอร์ และคาร์บอนิล หลังจากการดัดแปร เอเอฟเอ็ม เพื่อศึกษาการเปลี่ยนแปลงลักษณะความขรุขระของผิวฟิล์ม เครื่องวัดค่ามุมสัมผัสและสารละลายไดน์ใช้ในการตรวจสอบค่าแรงตึงผิว หลังจากที่ดัดแปรผิวเอทีอาร์เอฟทีไออาร์สเปกโทรสโคปี และรามานสเปกโทรสโกปี ไม่สามารถตรวจวิเคราะห์หาการเปลี่ยนแปลงโครงสร้างทางเคมีหรือหมู่ฟังก์ชันได้เนื่องจากการดัดแปรพื้นผิวมีความลึกไม่เพียงพอ อย่างไรก็ตามเอเอฟเอ็ม สามารถตรวจสอบการเปลี่ยนแปลงลักษณะความขรุขระของผิว เครื่องวัดค่ามุมสัมผัสและสารละลายไดน์ สามารถตรวจสอบถึงความแตกต่างของค่าแรงตึงผิวได้

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Polyethylene terephthalate (PET) films from flexible packaging industry were modified by corona treatment in ambient atmosphere, production line speed 410, 210 and 150 m/min, with electrical power 6.7 and 9.0 KW, plasma treatment under vacuum with O_2 and Ar, production line speed 600 m/min electrical power 4.0 KW, and chemical treatment with the amino resin compound. The equipment used in this study are attenuated total reflectance-Fourier transform infrared spectroscopy (ATR FT-IR) and Raman spectroscopy for analyzing chemical structures or functional groups such as O=C–O and C=O after modification, atomic force microscopy (AFM) for determining the nanotopographical changes on polymer surface, contact angle and dyne solution for determining the surface tension. After surface modification attenuated total reflectance-Fourier transform infrared spectroscopy (ATR FT-IR) and Raman spectroscopy can't analyze the changes of chemical structures or functional groups due to the depth of modified surface not enough. However atomic force microscopy (AFM) observation showed the roughness changes, contact angle and dyne value showed the variation of surface tension.

Field of study Petrochemistry and Polymer Science ...... Student's Signature ....

Academic Year: 2011 .... Advisor's Signature ....

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CHAPTER I

INTRODUCTION

1.1 Purpose of investigation

Nearly all products are packaged at some point in their life-cycle. Plastic films are widely used in packaging, and continue to grow in use as more and more applications switch from rigid to flexible packages. Flexible packages generally take up much less space than the rigid structures they replace, especially before they are filled with product. They commonly require less material, as well. Therefore, switching from rigid to flexible packaging can provide significant economic savings in warehouse space and transportation, as well as in package cost. On the other hand, because flexible packaging does not usually have as much strength as rigid packaging, stronger distribution packaging may be required. Opening and reclosing of flexible packaging may also be less user-friendly, and consumers may perceive some types of products in flexible packaging as being lower in quality than equivalent products in rigid or semi-rigid packages.

Common flexible packaging forms include wraps, bags and pouches. In these packages, plastic films may be used alone or combined with paper and/or metal to serve the basic packaging functions of containment, protection, communication and utility in the delivery of quality products to the consumer. While plastic films are most often found in flexible package structures, they may also be used as a component in rigid or semi-rigid package structures, for example, as a liner inside a carton, or as lidding on a cup or tray.

The most common film used in packaging is low-density polyethylene (LDPE), defined broadly to include linear low-density polyethylene (LLDPE). Appreciable amounts of high-density polyethylene (HDPE), polypropylene (PP), polyvinyl chloride (PVC), polyvinylidene chloride (PVDC), polyethylene terephthalate (PET), polyamide (Nylon) and other plastics are also used [1].

Polyethylene terephthalate (PET) film is an important raw material for flexible packaging industry. PET has many advantages such as good mechanical strength, toughness, polishing resistance at elevated temperature and high melting temperature and inexpensive. But it is not appropriate for some applications. The relatively hydrophobicity of PET affects its wettability, printability and biocompatibility. Various modification techniques have been developed and applied for improving hydrophilicity of PET. Traditionally, a variety of surface modification techniques have been proposed and many of them are regularly employed on an industrial scale. Some of the most important surface modification techniques include corona discharge, plasma and chemical coating.

Corona and plasma treatments are used in many industries. The corona was produced from a corona discharge in ambient atmosphere by using high energy electromagnetic field. Thus, it can create oxygen-containing functional group at the surface. Corona treatment is used in continuous process which is suitable for industries. However, the operation cost is high. The plasma treatment utilizes a similar principle to that of the corona treatment. Plasma was generated by gas feeding in a high energy-electromagnetic field under a vacuum condition. However, the operation cost also high similar to corona treatment. The chemical treatments are divided into two main types; wet treatment and surface grafting. These treatments have been purposed to resolve problems associated with undesirable properties of the polymer.

1.2 Research objectives

The objective of this research is to characterize the surface-modified PET film from industry. The equipment used in this study are attenuated total reflectance-Fourier transform infrared spectroscopy (ATR FT-IR) and Raman spectroscopy for analyzing chemical structures or functional groups after modification, and atomic force microscopy (AFM) for determining the nanotopographical changes on the polymer surface. Contact angle and dyne solution for determining the surface tension.

1.3 Scope of investigation

1. Comparison the chemical changes of PET film under corona treatment, plasma treatment and chemical treatment by using ATR FT-IR and FT-Raman spectroscopy.
2. Comparison the nanotopography changes of PET film after modified under corona treatment, plasma treatment and chemical treatment by using atomic force microscopy (AFM).
3. Comparison the surface tension of PET film after modified under corona treatment, plasma treatment and chemical treatment by using contact angle and dyne solution.

CHAPTER II

THEORY AND LITERATURE REVIEWS

2.1 Poly (ethylene terephthalate) or PET

PET is usually produced by a condensation polymerization of dimethyl ester of terephthalic acid and ethylene glycol. The PET structure containing aromatic ester units is shown in figure 2.1.

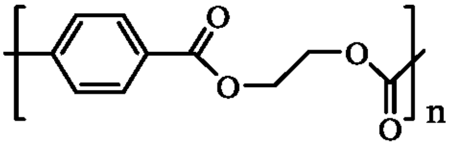

Figure 2.1 The PET structure.

PET has many advantages such as good mechanical properties, and heat resistance. Therefore, it is used in various industries such as textile industries, food packaging, and general purpose.

Polyethylene terephthalate is formed by condensation polymerisation of monoethylene glycol and purified terephthalic acid or dimethyl terephthalate. PET has good barrier properties, especially for gas. The barrier properties can be improved by metallize process. Typical PET properties are listed in table 2.1.

Table 2.1 Typical properties of poly (ethylene terephthalate) film [1].

Property	PET Polymer	
	Unoriented	Oriented
T_g (°C)	73-80	73-80
T_m (°C)	245-265	245-265
Heat distortion temperature, at 455 kPa (°C)	38-129	
Density (g/cm^3)	1.29-1.40	1.40
Tear modulus (GPa)	2.8-4.1	
Tear strength (MPa)	48-72	220-270
Elongation (%)	30-3,000	70-110
WVTR, at 37.8 °C and 90% RH (g μm/m^2 d)	390-510	440
O_2 permeability, at 25 °C (10^3 cm^3 μm/m^2 d atm)	1.2-2.4	1.1

2.2 Biaxially-oriented PET (BOPET) film processing

Orientation of plastic films improves some of the physical properties such as tensile strength, impact strength, clarity and stiffness. And also improvement in gas and water vapor barrier properties.

The first step of processes for plastics film is often extrusion. Chips are fed from a hopper into the barrel of the extruder then melted by heat and the mechanical action of the screw. The action of the screw forces the molten plastic through to a die. The shape of the die determines the type of product produced. An alternative die design will create thin flexible plastics films of the type used for foods packaging. [15].

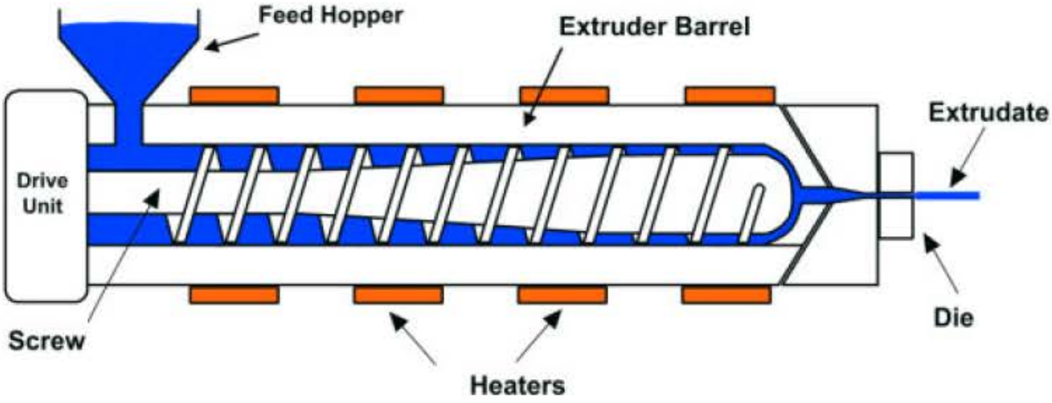

Figure 2.2 Extrusion [15].

Packaging film can be produced by extrusion followed by cooling on chill rolls. During the production process, cast film can be oriented by stretching. This strengthens the film and can also improve the gas permeation. Orientation can be in one direction only (uniaxial orientation) figure 2.3, or on both directions (biaxial orientation) [15]. Stretching is achieved by diverging the clips in machine and transverse direction on a closed loop figure 2.4 [16].

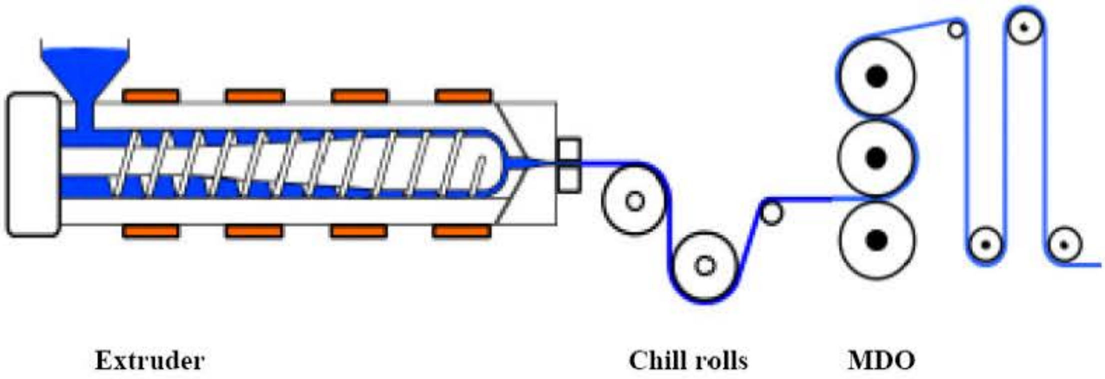

Figure 2.3 Extrusion casting and stretching [15].

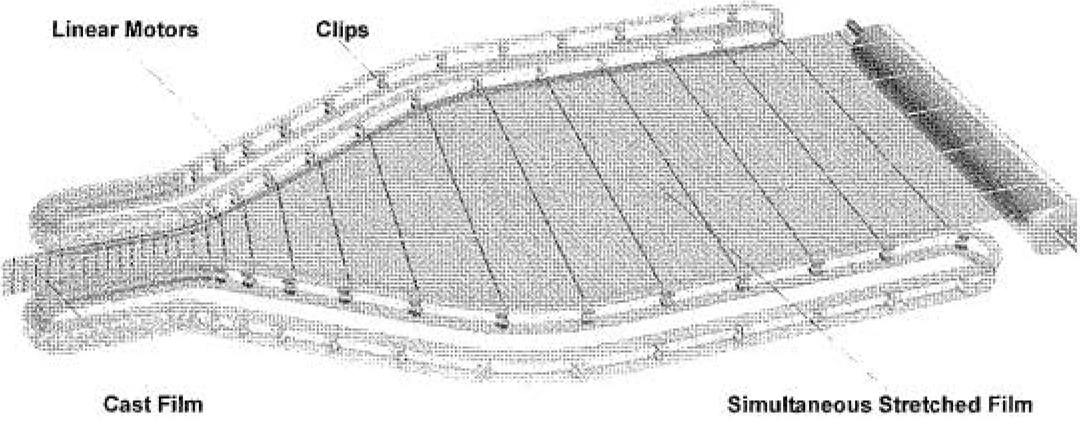

Figure 2.4 Transverse direction stretching [16].

2.3 Surface modification techniques

Modifications of plastic films are generally used to improve mechanical or physical properties so that the films are suitable for certain applications. This can be achieved by subjecting the films to mechanical or chemical treatments. Thus, surface treatments modify the surface topography, increase the surface energy and remove contaminants. Removal of contaminants is necessary for good adhesion of the surface to other substrates. A number of surface modification techniques, such as plasma, corona discharge and chemical treatments.

Plasma treatment is one of the most effective methods of surface modification of polymeric materials. The plasma activates gas molecules, such as oxygen and nitrogen. The activated species interact with the polymer's surfaces. The plasma process removes organic contaminants such as residual organic solvents. These surface contaminants undergo repetitive chain scission under the influence of ions, free radicals and electrons of the plasma until their molecular weight is sufficiently low to volatilize in the vacuum [1,13].

Corona treatment technique, a sufficiently high-voltage electrical discharge is applied to the surface of a moving substrate. The level of treatment is governed by the generator output and the speed of throughput. The corona treatment functions at atmospheric pressure and relatively high temperature. In this case, very significant surface oxidation occurs.

Chemical modification of the surface of polymers is an attractive method of improving the barrier characteristics of polymers. This modification can be achieved by reacting the polymer on the film surface. In some applications, the acidity of the primary film former or other components of the formulation will be sufficient to catalyze the reaction of partially alkylated and high imino (-NH) melamine resins. [1,19].

2.3.1 The corona treatment

The corona treatment is used to increase the wetting power and the adhesiveness on the surface of web film. The corona treatment activates the atmosphere and discharges electrons to oxidize the uppermost atomic layers of the web surface. Increasing the oxidation increases the surface energy. The created functional groups are polar which in turn create adhesive centers the applied printing inks, lacquers and adhesives [10].

2.3.1.1 System description

The system generally consists of the following components:

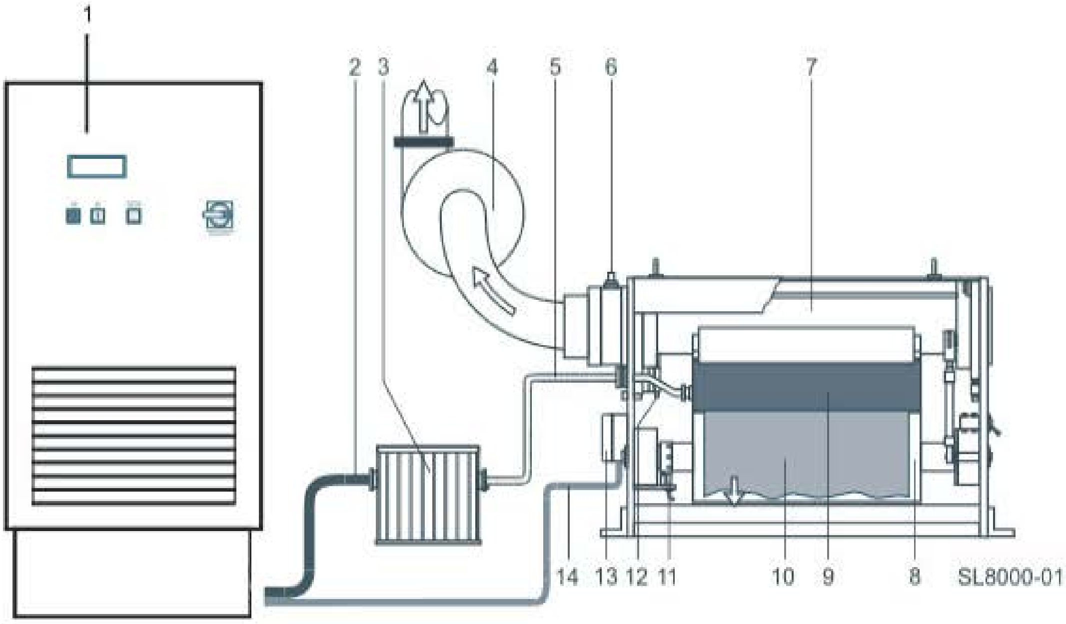

Figure 2.5 Corona system description [10].

Description of items in figure 2.5

1	Corona generator
2	Transformer connecting cable
3	High-voltage transformer
4	Exhaust system
5	Electrode connecting cable
6	Air-vane switch
7	Corona station
8	Carrier roll
9	Corona electrode
10	Web
11	Speed control
12	Electrode limit switch
13	Connector box
14	Control cable

2.3.2 The plasma treatment

2.3.2.1 Pretreatment station

The pretreatment station (glow station) is used to modified the film's surfaces, for better adhesion of the deposited layers. The central component of the pretreatment station is the Magnetron glow cathode. The pretreatment station is placed before the coating station of metallizing.

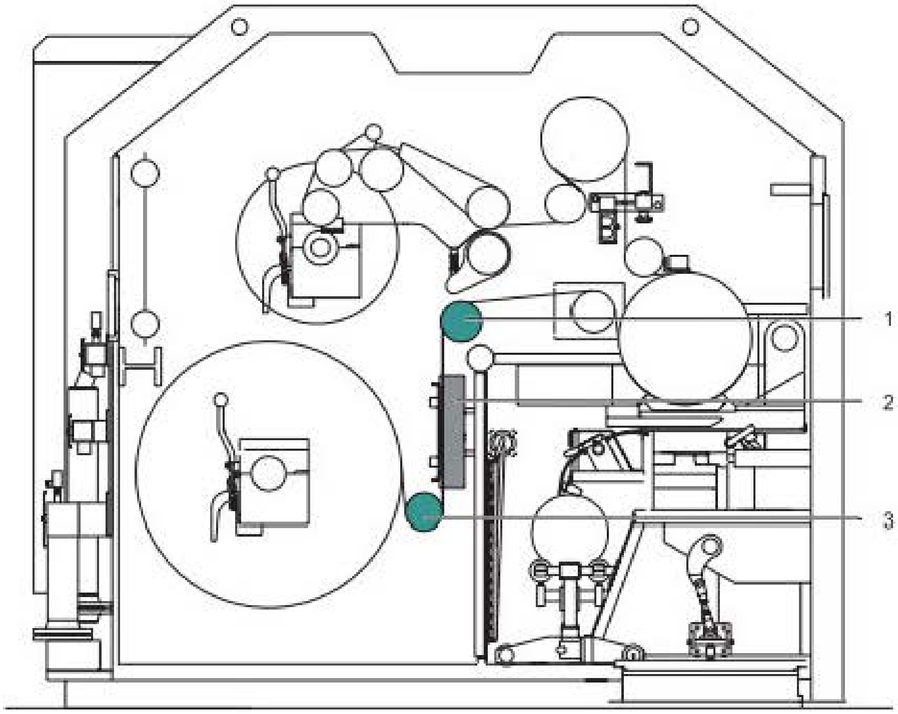

Figure 2.6 Plasma pretreatment station [12].

Description of items in figure 2.6

1	Spreader roll to spread the film web to be flat.
2	Cathode
3	Guide roller ensures the film runs along the pretreatment station without folds or contact.

2.3.2.2 Gas system

The process gases required for glowing are argon (Ar) and oxygen (O_2). The gases can be used separately (only Ar or O_2), or as a gas mixture (Ar + O_2). These process gases are used as follows:

- Argon Required to condition the cathode.
- Oxygen Primarily used only to pretreat the film.
- Oxygen + Argon Primarily used to clean and pretreat the film.

The process gases flow from the gas bottles via separate supply lines past a gas flow controller and then directly to the gas inlet of the glow cathode.

2.3.2.3 Body of the cathode

The following diagram shows the mechanical structure and main parts of the Magnetron glow cathode.

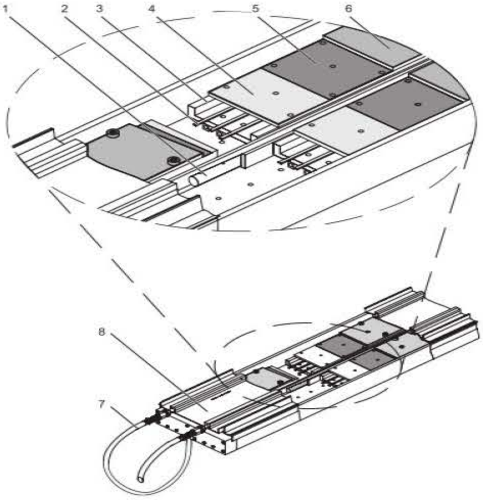

Figure 2.7 Body of the cathode [12].

Description of items in figure 2.7

1	Gas distribution tube
2	Magnets
3	Body of the cathode
4	Cooling plate

5	Graphite film
6	Target
7	Cooling water connection
8	Cathode lid

2.3.3 The coating treatment

2.3.3.1 Construction of coating unit

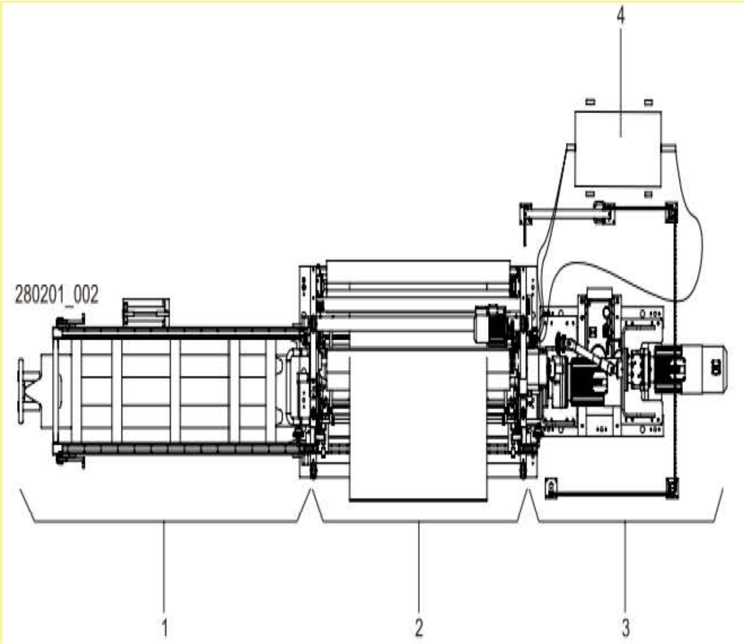

Figure 2.8 Top view of coating unit structural components [11].

Description of items in figure 2.8

1	Trolley receiving frame
2	Coating unit
3	Drive block with protective fence
4	Mass carriage Coating Unit

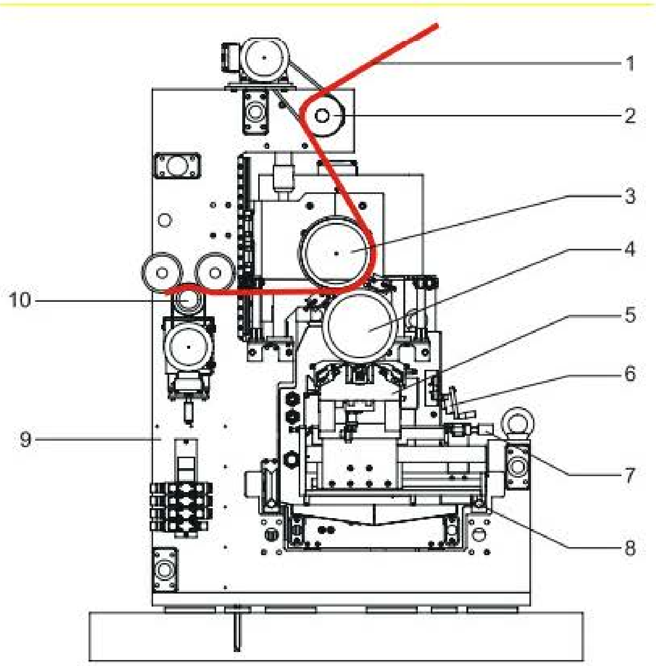

Figure 2.9 Coating with pressure roller [11].

Description of items in figure 2.9

1	Substrate web
2	Spreader roller
3	Pressure roller
4	Gravure roll
5	Mass solution transfer unit
6	Mass solution transfer unit adjusting vertical
7	Mass solution transfer unit adjusting horizontal
8	Rail guide of trolley
9	Machine frame work
10	Smoothing station

2.3.3.2 Coating unit

The coating unit is used for single-sided coating of running substrate-webs. The coating unit consists of the drive console, the base frame and a mobile trolley. The trolley contains the coating system with the mass solution transfer head . The trolley can be moved out of the base frame shown in figure 2.10.

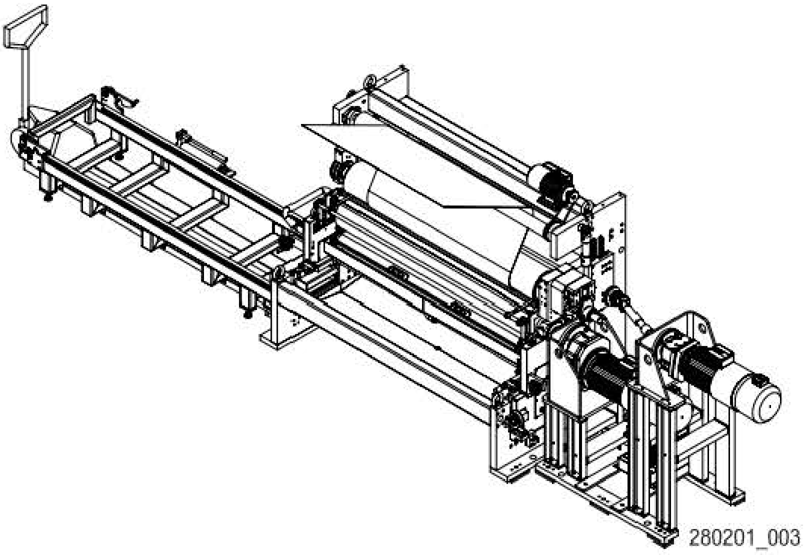

Figure 2.10 Web route, coating application [11].

2.2.3.3 Mass transfer head

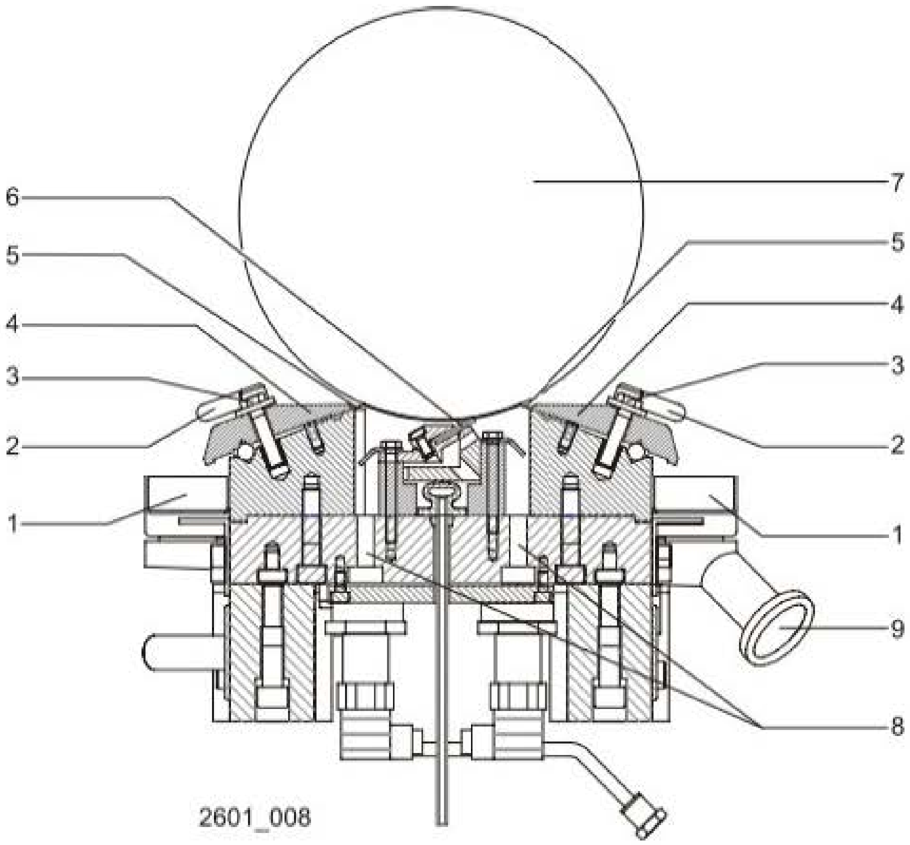

Figure 2.11 Mass transfer head construction [11].

Mass transfer head construction

1	Collecting solution
2	Handle
3	Screws of doctor blade clamping
4	Doctor blade clamping
5	Doctor blade
6	pneumatically adjustable
7	Gravure roll
8	Mass solution supply
9	Mass solution return connection

The mass solution transfer head is connected with the mass solution supply system via the supply and return connections. The coating system is supplied with mass solution via pumps. Wetting of the gravure roll is effected by the mass solution transfer head directly with the gravure rolls running in opposite direction to the web direction.

The mass solution fills the recesses of the gravure roll. Doctor blades scrape the excessive mass from the gravure roll. The doctor blades are pressed against the gravure roll. The pressure roller must cover the coating width shown in figure 2.12.

Figure 2.12 Rubber roll.

The coating quantity depends on:

- the type and quantity of cell of the gravure roll
- the viscosity of the coating solution
- the production line speed
- the relative speed of the gravure roll with line speed
- the hydrophilic or hydrophobic substrate

2.4 Spectroscopic characterization techniques

Generally, a simple transmission experiment is widely used in the analysis. It provides spectral information of the sample which is related to chemical structure and chemical composition. The simple transmission technique is not suitable for surface analysis. As a result, the reflected radiation and scattered radiation are employed for surface analysis and opaque samples. The ATR FT-IR and FT-Raman are the spectroscopic techniques for the measurement of the internal reflected radiation and scattered radiation, respectively.

2.5 Atomic force microscopy

AFM provides a number of advantages over conventional microscopy techniques. AFMs probe the sample and make measurements in three dimensions, x, y, and z, thus enabling the presentation of three-dimensional images of a sample surface. This provides a great advantage over any microscope available previously. With good samples , resolution in the x-y plane ranges from 0.1 to 1.0 nm and in the z direction is 0.01 nm. Contact mode AFM is one of the more widely used scanning probe modes, and operates by rastering a sharp tip across the sample. An extremely low force is maintained on the cantilever, thereby pushing the tip against the sample as it rasters. Either the repulsive force between the tip and sample or the actual tip deflection is recorded relative to spatial variation and then converted into an analogue image of the sample surface [18].

2.6 Contact Angle

The contact angle is a measure of the ability of a liquid to spread on a surface of non-treated and treated film. To Determine surface energy/surface tension with the shape of a drop placed on the surface. The contact angle is linked to the surface energy and surface tension [21].

2.7 Literature reviews

Zhang and Fang (2009) studied plasma surface treatment of polyester fabrics in composite atmosphere with air and 10% Ar under different experimental conditions. After plasma treatment the samples were printed with pigment inks. The results show that surface modified polyester fabrics exhibited enhanced color yields and excellent pattern sharpness. SEM and XPS analyses indicated that this improved color performance was mainly contributed by not only the etching effect but also oxygen containing polar groups induced onto fiber surfaces through plasma treatment.

Pandiyaraj et al. (2009) studied the adhesive properties of the plasma modified polypropylene (PP) and polyethylene terephthalate (PET) film surfaces. Hydrophilicity of these polymer film surfaces was studied by contact angle measurements. The chemical composition of the polymer films was analyzed by X-ray photoelectron spectroscopy (XPS). Atomic force microscopy (AFM) was used to study the changes in surface feature of the polymer surfaces. The adhesion strength of the plasma modified film was studied by T-peel strength test. The results showed a considerable improvement in surface wettability even for short exposure times. The AFM and XPS analyses showed changes in surface topography and formation of polar groups on the plasma modified PP and PET surfaces. These changes enhanced the adhesive properties of polymer film surfaces.

Esena et al. (2008) studied the plasma interaction with the surface produces modifications of its chemical structure or morphology. Surface modifications through cold plasma. The present work shows the surface modification of polyethylene terephthalate (PET) films after the exposure both to low-pressure plasma (film deposition by plasma enhanced chemical vapour deposition) and to an atmospheric pressure dielectric barrier discharge (surface etching). For the atmospheric pressure plasma-treated samples, contact angle and atomic force microscope analysis enable us to determine roughness changes. For the low-pressure plasma samples, contact angles and Fourier transform infrared absorption spectroscopy analysis are used to estimate the chemical composition. Both plasma treatments (film deposition and etching) cause changes in optical properties as indicated by reflectivity measurements.

Pandiyaraj et al. (2008) studied in the present work, Poly (ethylene terephthalate) films have been exposed to glow discharge air plasma to improve their surface properties for technical applications. Surface energy values have been estimated using contact angle value for different exposure times and different test liquids. Surface composition and morphology of the films were analyzed by XPS and AFM. Crystallinity of the plasma treated samples were studied by XRD analysis. The improvement in adhesive strength was studied by measuring T-peel strength and lap shear strength tests. It was found that the plasma treatment modified the surfaces both in chemical composition and morphology. Change of chemical composition made the polymer surfaces to be highly hydrophilic, which mainly depends on the increase in oxygen-containing groups. The AFM and XRD observation showed that the surface roughness and crystallinity of the PET film increased due to plasma treatment.

Laskarakis et al. (2007) studied improvement the production of Flexible Electronic Devices (FEDs) by plasma treatment in large-scale manufacturing processes. Plasma treatment can be successfully employed for the improvement of the bonding structure and surface properties of flexible polymeric substrates. In this work report on the effect of Pulsed DC N + ion bombardment using different ion energies, on the bonding structure, electronic and optical properties and surface nanotopography of Poly(Ethylene Terephthalate) (PET) substrates. For the investigation of the optical properties, then have used in-situ and real-time Spectroscopic Ellipsometry from the IR to Vis-far UV spectral region, in combination to advanced modelling procedures, whereas Atomic Force Microscopy has been employed for surface nanotopography investigation. As it has been found, the N + bombardment leads to the appearance of new chemical bonds (C=N or C=O), as well as partial disappearing of the C–O bond of ester group, on a surface layer of PET.

Mirabedini et al. (2007) studied Low-pressure plasma treatments in an of discharge of O_2 and Ar were employed to introduce polar functional groups onto the biaxial-oriented polypropylene (BOPP) surfaces to enhance the wettability and activation. The effects of plasma treatment on the morphology and wettability of the BOPP films were characterized using static contact angle measurements, attenuated total reflection (ATR)–FTIR spectroscopy, scanning electron microscopy (SEM) and atomic force microscopy (AFM). A clear increase in the surface energy of BOPP films due to O_2 and Ar plasma treatments was observed. The surfaces became highly hydrophilic when exposed for 20 s or longer to the plasma discharge. The wettability of polymer surface can be improved when oxygen functionalities are generated, which can be achieved directly in O-containing plasmas or via post plasma reactions. Small reduction in surface energy of plasma treated BOPP films, after 30 days aging showed that the plasma-induced cross-linking in BOPP film was not the dominant phenomena. With increasing the treatment power and time, rate of the decrease in surface energy after aging is reduced. AFM and SEM images revealed distinct changes in the topography of BOPP due to O_2 and Ar plasma treatments. Nodular structure is formed on the BOPP film during the treatment and the size of the nodules increases with the treatment time.

Meiron and Saguy (2007) studied a top-view vibration system for measuring the apparent contact angle corresponding to the global energy minimum was applied in quantifying the effect of plastic film, roughness, and surface treatment on wettability. Liquids representing typical pure liquids (diiodom ethane, ethylene glycol) and food products (10% ethanol, 3% fat milk, 10% sucrose, triolein) were tested on low linear density polyethylene (LLDPE) and polyethylene terephthalate (PET), exposed, or not, to commercial corona discharge treatment (CDT). Apparent contact angle values increased with surface tension of the liquid. The major effect of CDT was to enhance surface polarity by significantly increasing the polar component of surface free energy.

Ardelene et al. (2005) studied Chemical functionalities, topography and adherence between Al and polyethylene terephthalate (PET) films, modified by laser treatment below the polymer ablation threshold fluence in air and in helium at different wavelengths, fluences, pulse numbers and by low pressure plasma treatment in He 95% with O_2 5%, at 0.2 W/cm^3 were investigated by XPS, AFM, water contact angle and adhesion measurements. XPS results revealed formation of polar-oxygenated functional groups (C=O, O–C=O) by laser treatments in air and (ii) incorporation of ester and ether groups by plasma treatment in He 95% with O_2 5%. After deposition of thermally evaporated Al on laser or plasma treated PET films, U-Peel tests indicated that laser treatment in air at 248 nm and 20 mJ/cm^2, and plasma treatment improved Al/PET adhesion. XPS studies revealed the presence of an increasing number of Al–O–C stable and cohesive interfacial complexes formed by chemical interaction between aluminium and the laser treated in air or plasma treated in He 95% with O_2 5% PET films. These interfacial compounds play an important role in the enhancement of the metal/polymer adhesion.

CHAPTER III

EXPERIMENT

3.1 Instrument

1. FT-IR spectrometer equipped with a mercury cadmium-telluride (MCT) detector Nicolet 6700.
2. DXR Raman microscope thermo scientific
3. Atomic force microscope commercial SPA-400 (Seiko Instrument, Inc., Japan).
4. Contact angle.

3.2 Instruments and apparatus

1. Conventional ATR accessory: Single reflection attenuated total reflection (SATR) accessory (the Seagull^{TM}, Harrick Scientific, USA) equipped with a ZnSe IRE at the angle of incident of 45 degrees)
2. Homemade diamond μATR probe developed by Sensor Research Unit, Department of Chemistry, Faculty of Science, Chulalongkorn University, Bangkok 10330, Thailand
3. Homemade portable vertical contact angle.

3.3 Chemicals and materials

1. Formamide-AR grade ; Merck.
2. Ethyl cello solve-AR grade ; Fluka.
3. Distilled water.
4. De ionized water
5. PET film ; Polyplex (Thailand) Public Co., Ltd.

3.4 Sample preparation

3.4.1 PET film

The examined polymeric films were industrially supplied biaxially oriented PET films with thicknesses of 12-36 μm.

Table 3.1 Modification techniques parameters.

		Chemical		Plasma	Corona		
	Line Speed (m/min)	320	390	600	150	210	410
Current	KW	8 - 9		4	6 - 9		
Gas feeding	Oxygen (sccm)	-		800	Ambient		
	Argon (sccm)			600			

3.5 Characterization of modified PET films.

3.5.1 Surface analysis by ATR FT-IR and Raman spectroscopy technique.

3.5.1.1 ATR FT-IR spectroscopy

ATR spectra were recorded in the frequency ranging from 750 to 1800 cm^{-1} on Nicolet 6700 FT-IR spectrometer with a mercury-cadmium-tellurium (MCT) detector at resolution of 4 cm^{-1}. All samples were collected at 128 co-addition times. The ATR spectra of samples were acquired in the reflection mode of infrared microscope. A homemade diamond μATR probe, developed by Sensor Research Unit, Department of Chemistry, Faculty of Science, Chulalongkorn University, Bangkok 10330, Thailand,

Figure 3.1 ATR FT-IR microspectroscope: Continuμm^{TM} infrared microscopeattached to the Nicolet 6700 FT-IR spectrometer.

3.5.1.2 Raman microspectroscopy

A PET sample was placed on the tray, which is specifically designed for Raman characterization. The laser light from Raman spectrometer was focused on the sample. The focused point can be seen and adjusted through the camera that equipped with a computer. The PET specimen was subsequently collected by Raman spectrometer.

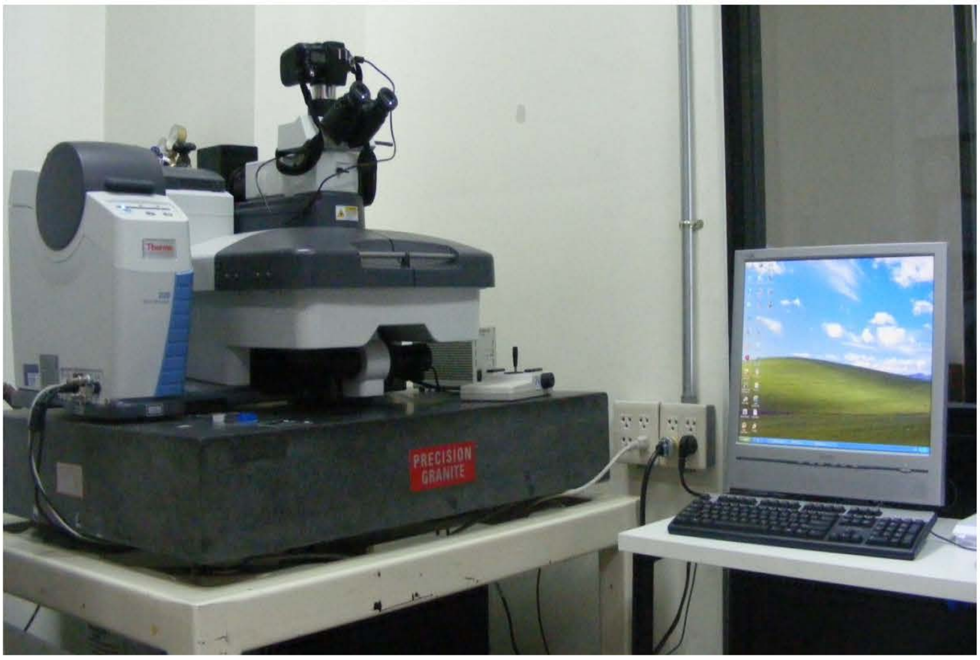

Figure 3.2 Thermo scientific DXR Raman microscope.

3.5.1.3 Curve fitting

The observed ATR FT-IR and Raman spectra were resolved by the curve fitting algorithm in the OMNIC software.

3.5.2 Surface morphology by atomic force microscope

Atomic force microscope (AFM) for the observation of the surface nanotopography was a commercial SPA-400 atomic force microscope (Seiko Instrument, Inc., Japan) with a calibrated 20 micrometer XY-scan and 10 micrometer Z-scan range PZT-scanner. AFM measurement was carried out in the non-contact mode using silicon tips with a force constant of 13 N/m and resonance frequency is 132 KHz in ambient air. All reported images were scanned with scan rates in the range of 0.5-1.0 Hz.

Figure 3.3 Commercial SPA-400 atomic force microscope.

3.5.3 Surface tension (dyne test)

Film surface tension was evaluated by using dyne solution test following the guideline given by ASTM D 2578-04.

Table 3.2 Surface tension test solution preparation method [17].

Dyne value	Formamide-AR grade (ml)	Ethyl cello solve-AR grade (ml)	Distilled water (ml)
38	27.0	23.0	-
40	31.5	18.25	-
42	35.75	14.25	-
44	39.0	11.0	-
46	41.5	8.5	-
48	43.5	6.5	-
50	45.35	4.65	-
52	46.85	3.15	-
54	48.25	1.75	-
56	49.5	0.5	-
58	50	0	-
60	32.5	-	17.5
62	23.5	-	26.5
64	15.3	-	34.7
66	9.1	-	40.9

3.5.4 Contact Angle

Film surface wettability was evaluated by using contact angle following the guideline given by ASTM D 724-99.

ค่ามุมสัมผัส 59.6

Figure 3.4 Portable vertical contact angle.

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Surface analysis by ATR FT-IR and Raman spectroscopy techniques

4.1.1 ATR FT-IR

ATR FT-IR spectra of the corona treated PET films and the non-treated films are illustrated in Figure 4.1. For the ATR FT-IR spectra of the non-treated and the corona treated films, show peaks at the area of ~1710–1720 cm^{-1} is related to the C=O stretching bond, the peak at 1505 cm^{-1} is C-H deformation mode, the peaks at ~1470 and 1340 cm^{-1} are C-H_2 bending and wagging mode, the peaks at ~1024 and 1408 cm^{-1} are the C–H bond deformation of the parasubstituted benzene rings, the peak at 1255 cm^{-1} is ester group, the peak at 1020 cm^{-1} is C-H benzene ring deformation and the peak at ~970 cm^{-1} is C–O stretching vibration, respectively [4, 14]. The band assignments of PET were shown in table 4.1.

The spectra can't specified the new chemical structure or functional group because of corona treated PET films and the non-treated films are shows the peaks at the same wavenumber (cm^{-1}).

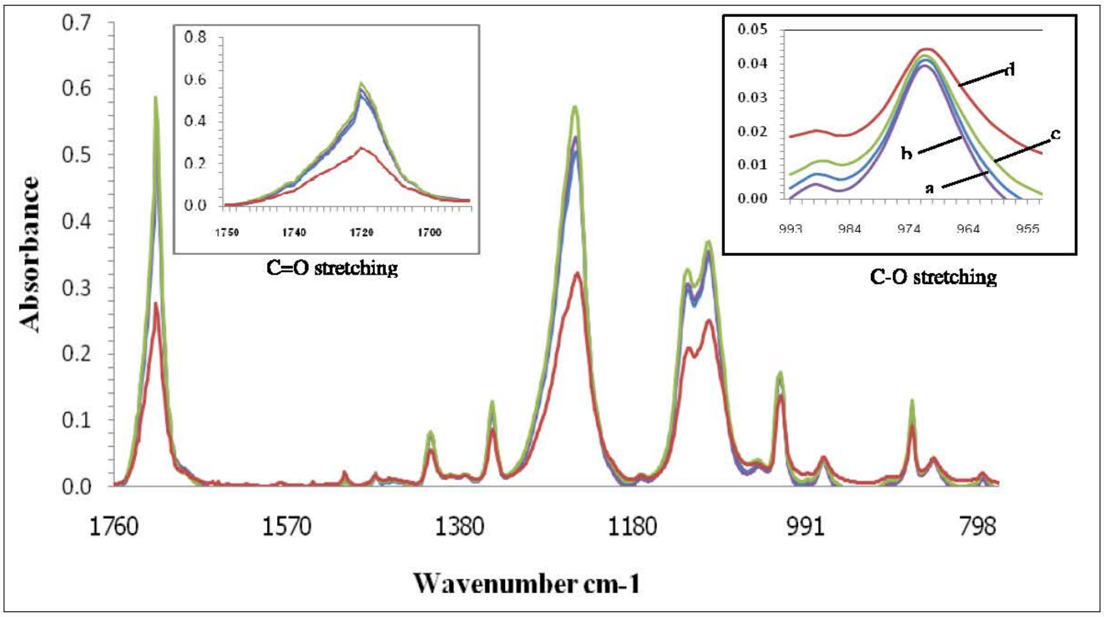

Figure 4.1 The ATR FT-IR spectra of non-treated and corona-treated PET films (a) non-treated, (b) corona treated 1, line speed 410 m/min, 9 KW, (c) corona treated 2, line speed 210 m/min, 9 KW, (d) corona treated 3, line speed 150 m/min, 9 KW.

Table 4.1 Infrared band assignments of PET [4].

Wave number (cm^{-1})	Bands assignment
1715	C=O stretching of aromatic ester
1613	C=C stretching vibration of aromatic ring
1578, 1505, 1408	Skeletal vibration of aromatic ring conjugation
1408, 1024	C-H deformation of parasubstituted benzene ring
1371, 1338	-CH_2- wagging
1255	Ester group stretching
1239, 1097	Asymmetric and symmetric stretching of C-O-C group of aromatic ester
1173, 1117, 1017	Skeletal ring indicated 1,4-substitution
970	C-O stretching vibration
871	C-H deformation of aromatic ring

The spectral of corona treated PET films show in figure 4.2 for C=O stretching at 1730-1710 cm^{-1} shows (a) non-treated, (b) corona treated 1, line speed 410 m/min, 9 KW, (c) corona treated 2, line speed 210 m/min, 9 KW, (d) corona treated 3, line speed 150 m/min, 9 KW at the same wavenumber (cm^{-1}) also in figure 4.3 for C-O stretching at 975-965 cm^{-1} and figure 4.4 for ester group at 1260-1240 cm^{-1}.

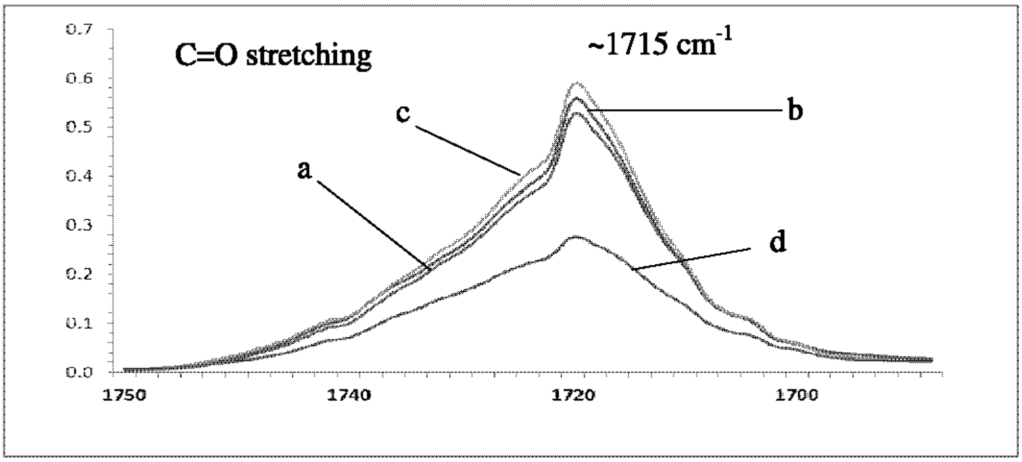

Figure 4.2 The ATR FT-IR spectral C=O stretching of non-treated and Corona treated PET films (a) non-treated, (b) corona treated 1, line speed 410 m/min, 9 KW, (c) corona treated 2, line speed 210 m/min, 9 KW, (d) corona treated 3, line speed 150 m/min, 9 KW.

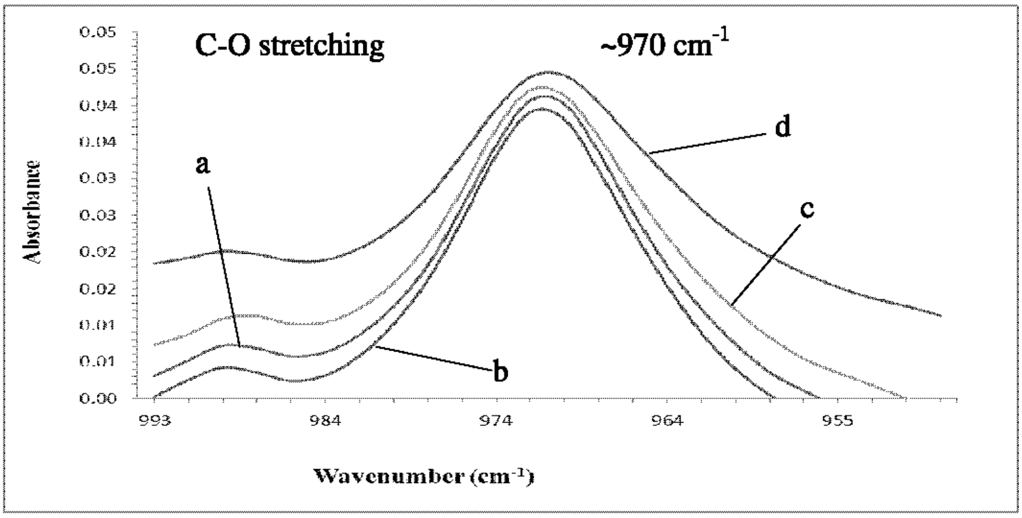

Figure 4.3 The ATR FT-IR spectral C-O stretching of non-treated and corona treated PET films (a) non-treated, (b) corona treated 1, line speed 410 m/min, 9 KW, (c) corona treated 2, line speed 210 m/min, 9 KW, (d) corona treated 3, line speed 150 m/min, 9 KW.

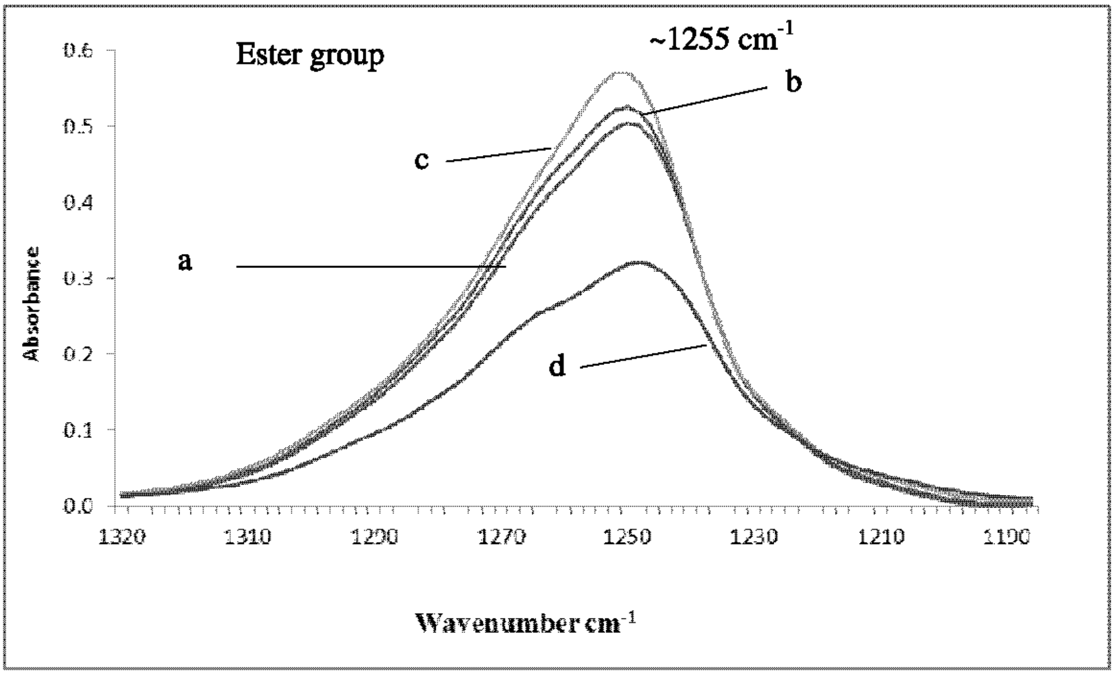

Figure 4.4 The ATR FT-IR spectral ester group of non-treated and corona treated PET films (a) non-treated, (b) corona treated 1, line speed 410 m/min, 9 KW, (c) corona treated 2, line speed 210 m/min, 9 KW, (d) corona treated 3, line speed 150 m/min, 9 KW.

ATR FT-IR spectra of the plasma treated PET films and the non-treated films are illustrated in figure 4.5. For the ATR FT-IR spectra of the non-treated and the plasma treated films, show peaks at the area of ~1710–1720 cm^{-1} is related to the C=O stretching bond, the peak at 1505 cm^{-1} is C-H deformation mode, the peaks at ~1470 and 1340 cm^{-1} are C-H$_2$ bending and wagging mode, the peaks at ~1024 and 1408 cm^{-1} are the C–H bond deformation of the parasubstituted benzene rings, the peak at 1255 cm^{-1} is ester group, the peak at 1020 cm^{-1} is C-H benzene ring deformation and the peak at ~970 cm^{-1} is C–O stretching vibration, respectively [4, 14]. The band assignments of PET were shown in table 4.1.

The spectra can't specified the new chemical structure or functional group similar to corona treated PET films.

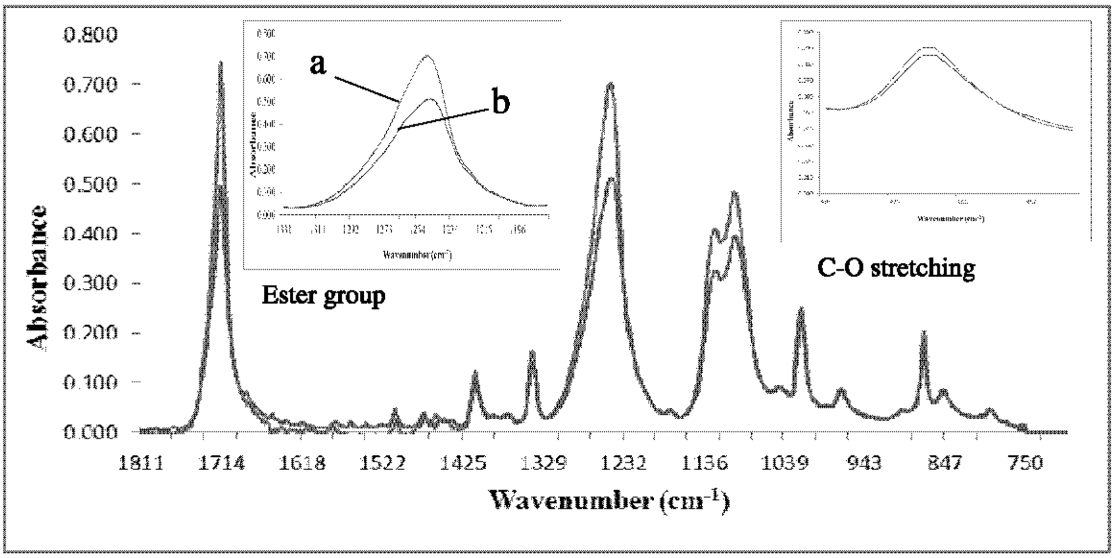

Figure 4.5 The ATR FT-IR spectra of non-treated and plasma treated PET films (a) non-treated, (b) plasma treated, line speed 600 m/min, 4 KW.

The spectral of plasma treated PET film show in figure 4.6 for C=O stretching at 1730-1710 cm^{-1} shows (a) non-treated, (b) plasma treated 1, line speed 600, m/min, 4 KW at the same wavenumber (cm^{-1}) also in figure 4.7 for C-O stretching at 975-965 cm^{-1} and figure 4.8 for ester group at 1260-1240 cm^{-1}.

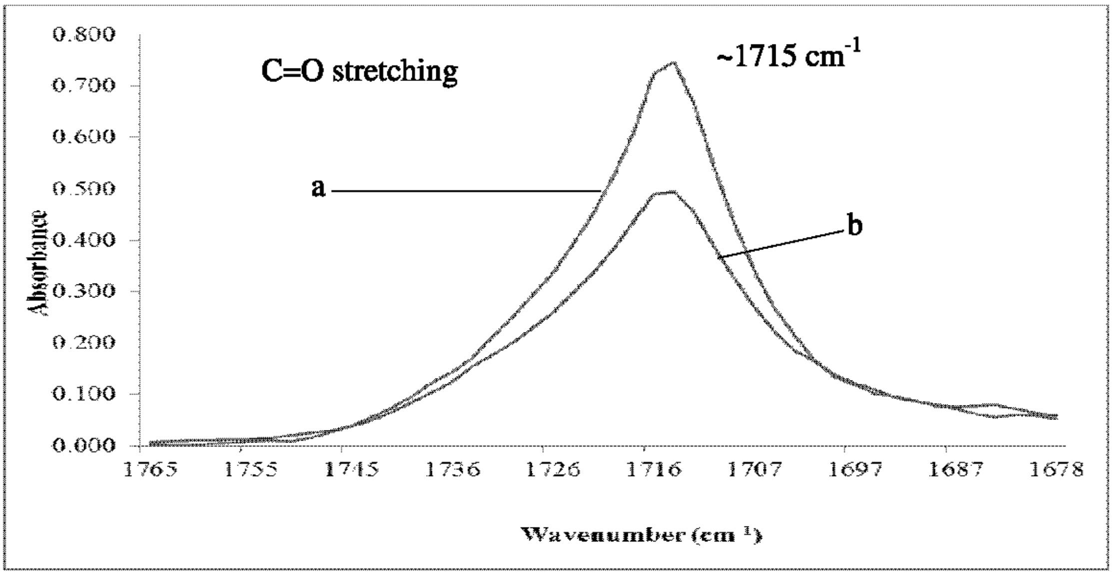

Figure 4.6 The ATR FT-IR spectral C=O stretching of non-treated and plasma treated PET films (a) non-treated, (b) plasma treated, line speed 600 m/min, 4 KW.

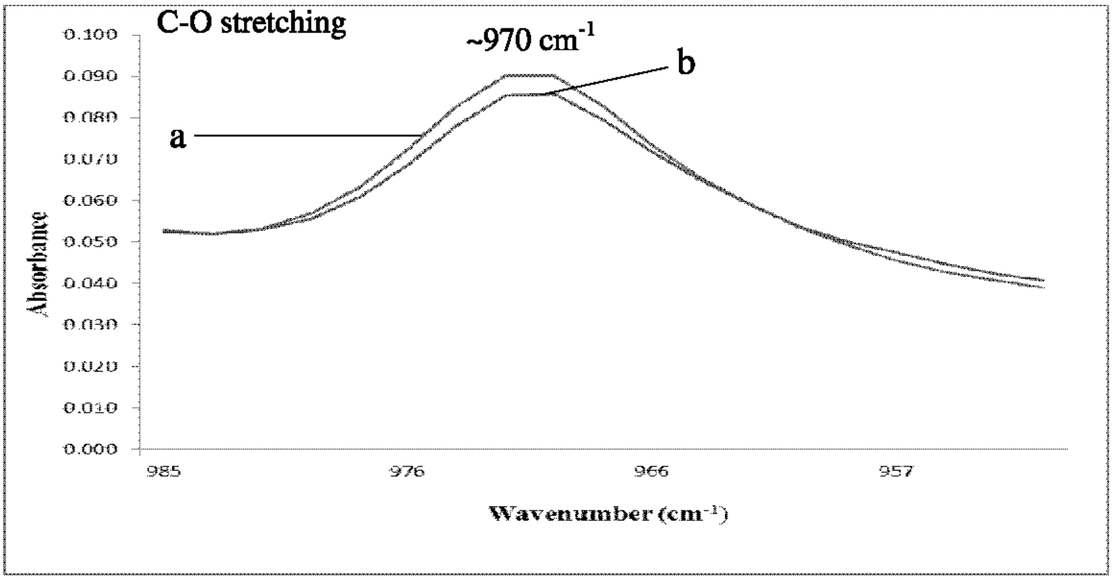

Figure 4.7 The ATR FT-IR spectral C-O stretching of non-treated and plasma treated PET films (a) non-treated, (b) plasma treated, line speed 600 m/min, 4 KW.

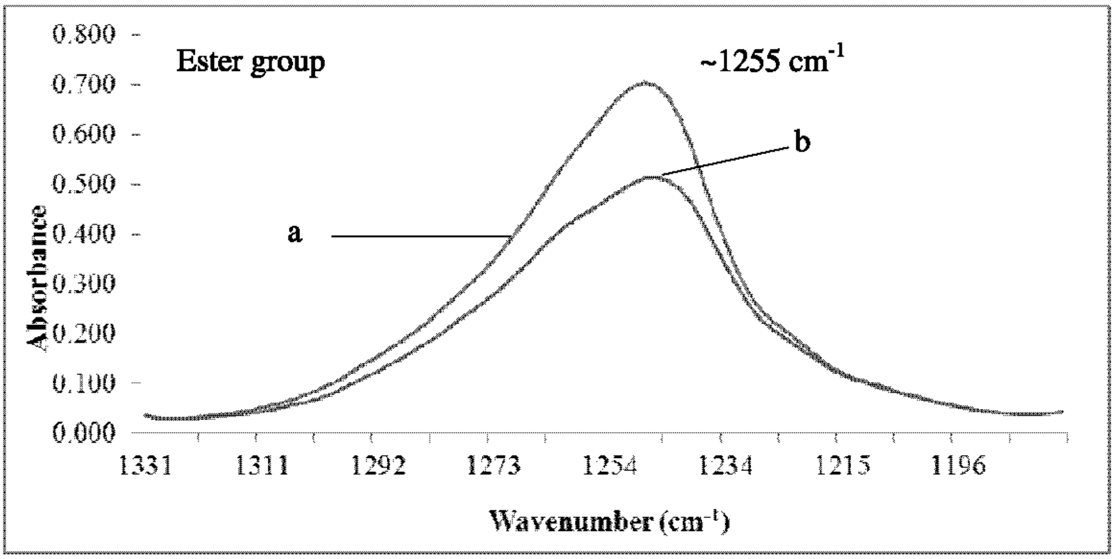

Figure 4.8 The ATR FT-IR spectral ester group of non-treated and plasma treated PET films (a) non-treated, (b) plasma treated, line speed 600 m/min, 4 KW.

ATR FT-IR spectra of the chemical treated PET films and the non-treated films are illustrated in Figure 4.9. For the ATR FT-IR spectra of the non-treated and the chemical treated films, show peaks at the area of ~1710–1720 cm^{-1} is related to the C=O stretching bond, the peak at 1505 cm^{-1} is C-H deformation mode, the peaks at ~1470 and 1340 cm^{-1} are C-H_2 bending and wagging mode, the peaks at ~1024 and 1408 cm^{-1} are the C–H bond deformation of the parasubstituted benzene rings, the peak at 1255 cm^{-1} is ester group, the peak at 1020 cm^{-1} is C-H benzene ring deformation and the peak at ~970 cm^{-1} is C–O stretching vibration, respectively [4, 14]. The band assignments of PET were shown in table 4.1.

The spectral of chemical treated PET film shows in figure 4.10 at 1130-1110 cm^{-1} and expect to amine group due to the coating solution have some part of amine compound.

The spectra can't specified the new chemical structure or functional group similar to corona treated and plasma treated PET films.

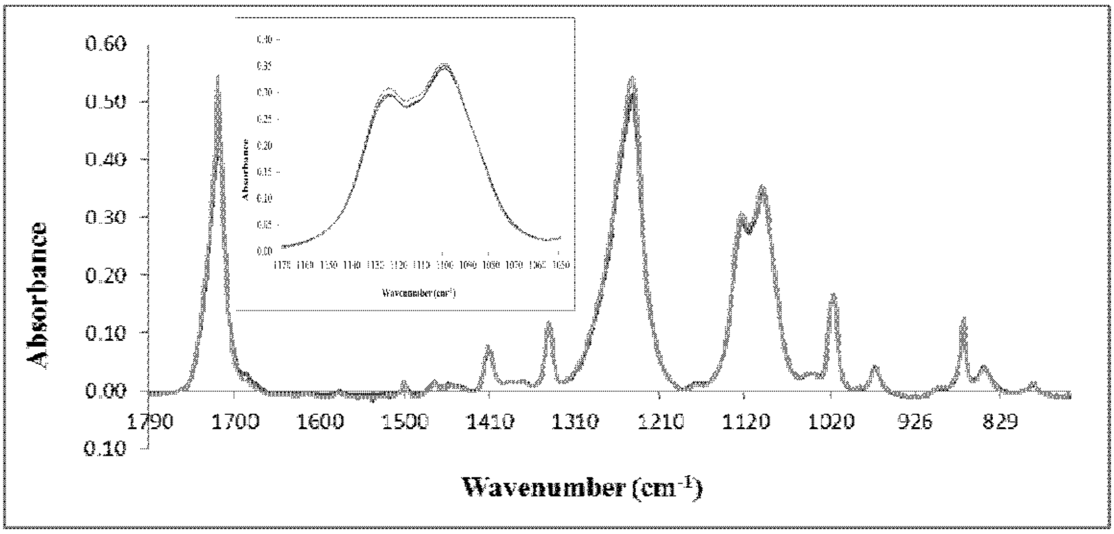

Figure 4.9 The ATR FT-IR spectra of non-treated and chemical treated PET films (a) non-treated, (b) chemical treated 1, line speed 390 m/min, (c) chemical treated 2, line speed 390 m/min.

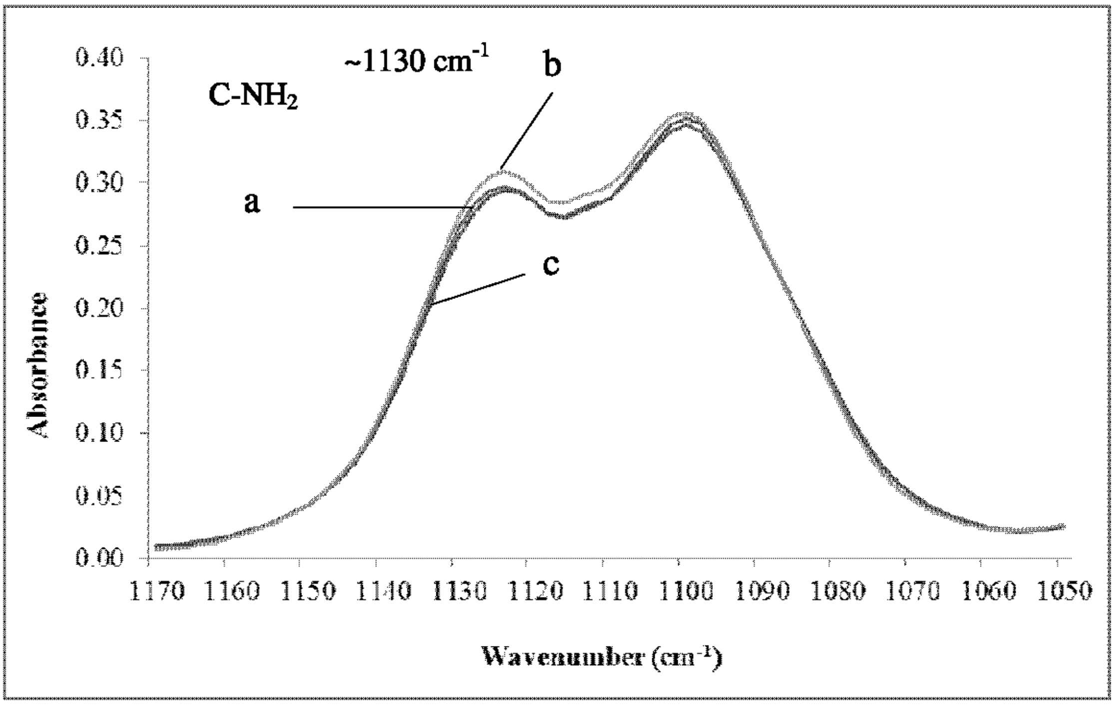

Figure 4.10 The ATR FT-IR spectral C-NH$_2$ of non-treated and chemical treated PET films (a) non-treated, (b) chemical treated 1, line speed 390 m/min, (c) chemical treated 2, line speed 320 m/min.

4.1.2 FT-Raman spectroscopy

Raman spectrum of corona treated PET film was collected by FT-Raman spectrometer. Peak assignments of PET are shown in table 4.2 [1-4]. The FT-Raman spectra of the corona treated PET film was compared with that of non-treated PET figure 4.11.

The spectra of corona treated PET film in figure 4.11 shows (a) non-treated, (b) corona treated 1, line speed 410 m/min, 9 KW, (c) corona treated 2, line speed 210 m/min, 9 KW, (d) corona treated 3, line speed 150 m/min, 9 KW at the same Raman shift (cm^{-1}) also in figure 4.12 for C=O stretching at 1730-1720 cm^{-1}, figure 4.13 for C-O stretching at 1290-1270 cm^{-1} and figure 4.4 for ester group at 1260-1240 cm^{-1}.

The spectra can't specified the new chemical structure or functional group.

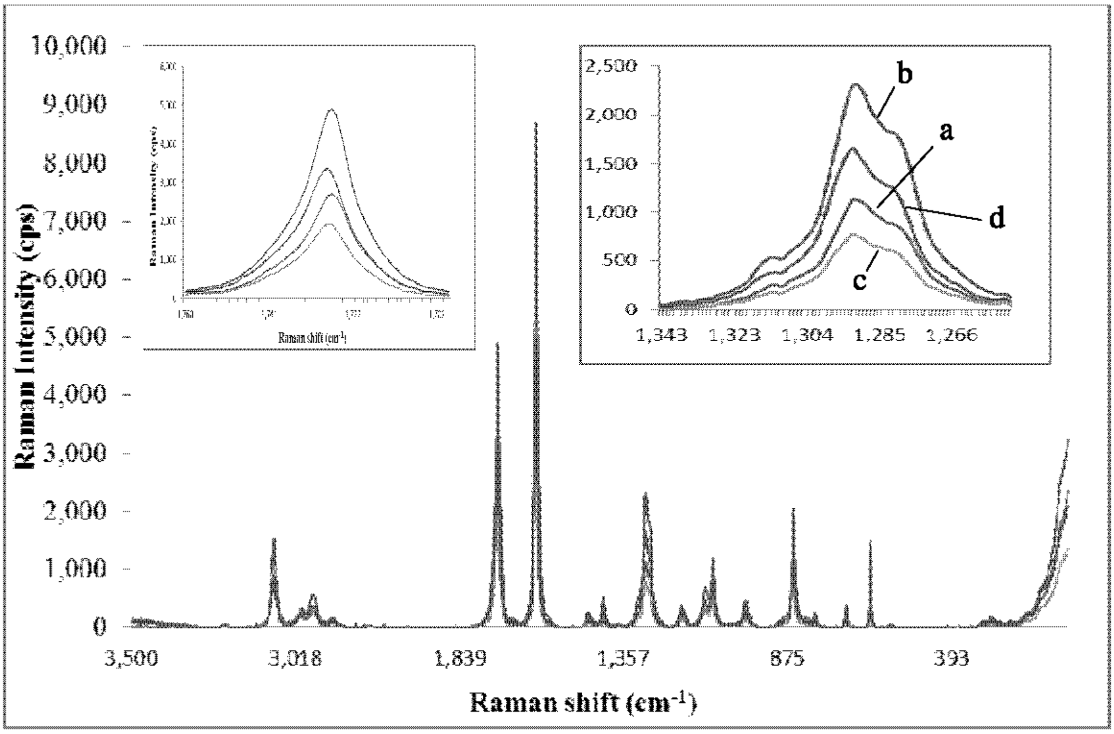

Figure 4.11 The Raman spectra of non-treated and corona treated PET films (a) non-treated, (b) corona treated 1, line speed 410 m/min, 9 KW, (c) corona treated 2, line speed 210 m/min, 9 KW, (d) corona treated 3, line speed 150 m/min, 9 KW.

Table 4.2 FT-Raman bands assignment of PET spectrum.

Raman shift (cm^{-1})	Bands assignment
3080	Aromatic C-H stretching
2964, 2907	Aliphatic C-H stretching
1726	C=O stretching
1614	C=C aromatic ring
1459	C-H deformation, residual glycol in PET film
1414	C-C stretching of aromatic ring
1372	CH_2 wagging
1288	Aromatic ring and O-C stretching
1184	C-H in plane bending of aromatic ring
1116, 1095	C-H in plane bending and C-O stretching
999	C-C stretching, glycol
857	C-C breathing
795	C-C out of plane of aromatic ring
703	C-C-C out of plane of aromatic ring
632	C-C-C in plane bending of aromatic ring

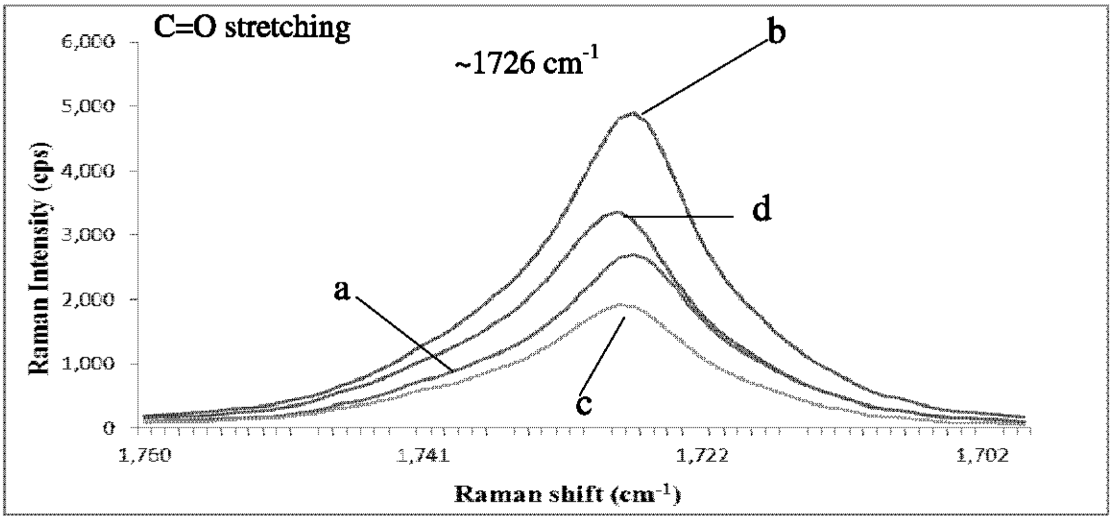

Figure 4.12 The Raman spectral C=O stretching of non-treated and corona treated PET films (a) non-treated, (b) corona treated 1, line speed 410 m/min, 9 KW, (c) corona treated 2, line speed 210 m/min, 9 KW, (d) corona treated 3, line speed 150 m/min, 9 KW.

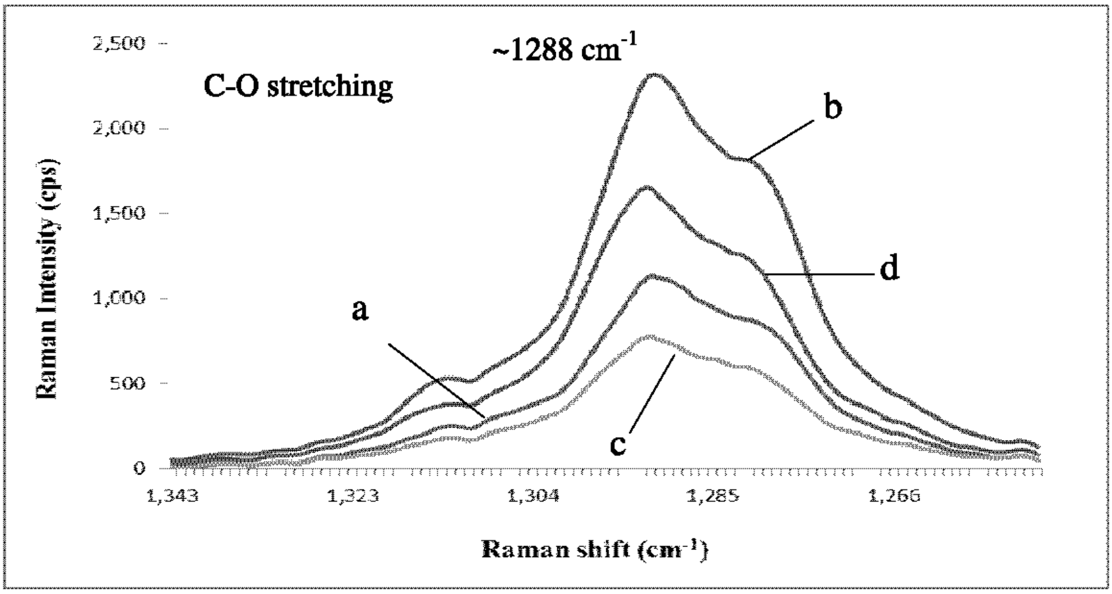

Figure 4.13 The Raman spectral C-O stretching of non-treated and corona treated PET films (a) non-treated, (b) corona treated 1, line speed 410 m/min, 9 KW, (c) corona treated 2, line speed 210 m/min, 9 KW, (d) corona treated 3, line speed 150 m/min, 9 KW.

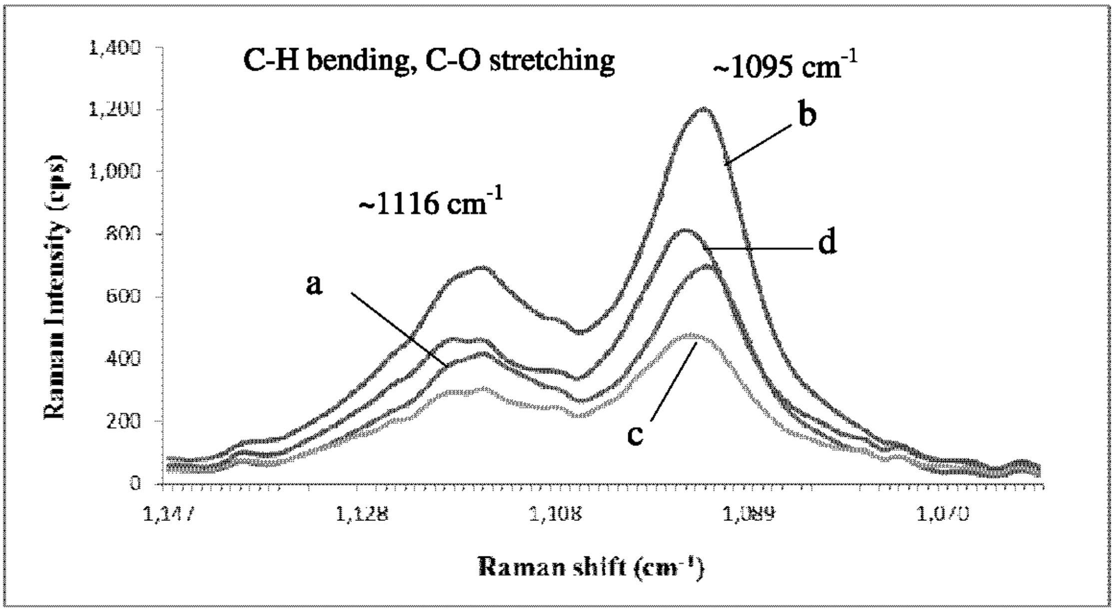

Figure 4.14 The Raman spectral C-H bending, C-O stretching of non-treated and corona treated PET films (a) non-treated, (b) corona treated 1, line speed 410 m/min, 9 KW, (c) corona treated 2, line speed 210 m/min, 9 KW, (d) corona treated 3, line speed 150 m/min, 9 KW.

4.2 Atomic force microscope (AFM)

The surface topography of non-treated and treated PET films were observed by AFM. Figure 4.15 shows the roughness of corona treated film 1-3 (b, c and d) are more than non-treated film (a) PET film. The surface roughness of the treated PET films increased as the treatment time increased (the treatment time increased as the production line speed reduced due to fixed the treatment power-KW), the corona treated PET films had inconsistency on roughness (comparison b, c and d) but got similar surface tension (dyne value 58-61), shows in table 4.3.

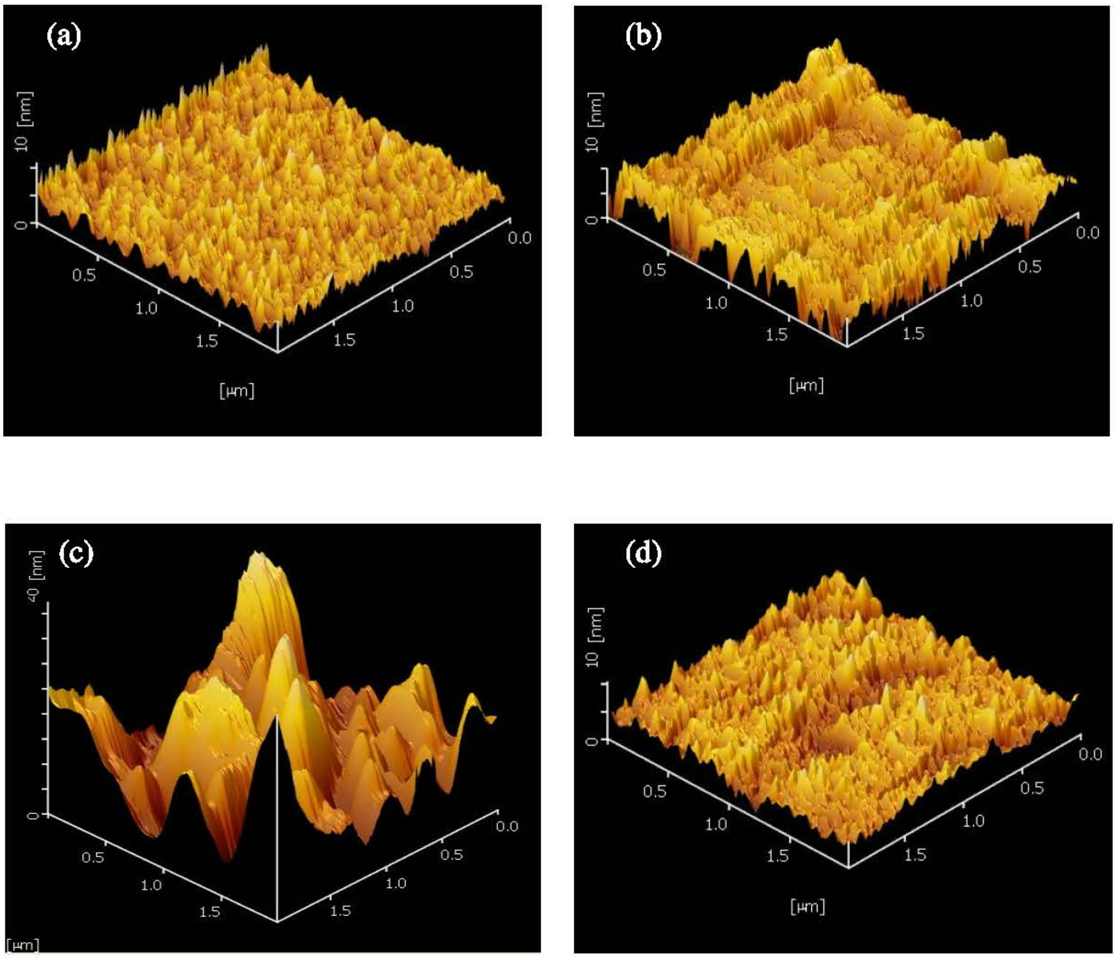

Figure 4.15 Surface nanotopography of PET films (a) non-treated, (b) corona treated 1, line speed 410 m/min, 9 KW, (c) corona treated 2, line speed 210 m/min, 9 KW, (d) corona treated 3, line speed 150 m/min, 9 KW.

Figure 4.16 shows the roughness of corona treated 4 (c) has smoother than corona treated 1 (b) due to low treatment power (6.7 and 9.0 KW) but similar the line speed but got similar surface tension (dyne value 58-61), shows in table 4.3. From this result the treatment power can be reduce to the suitable conditions for energy saving.

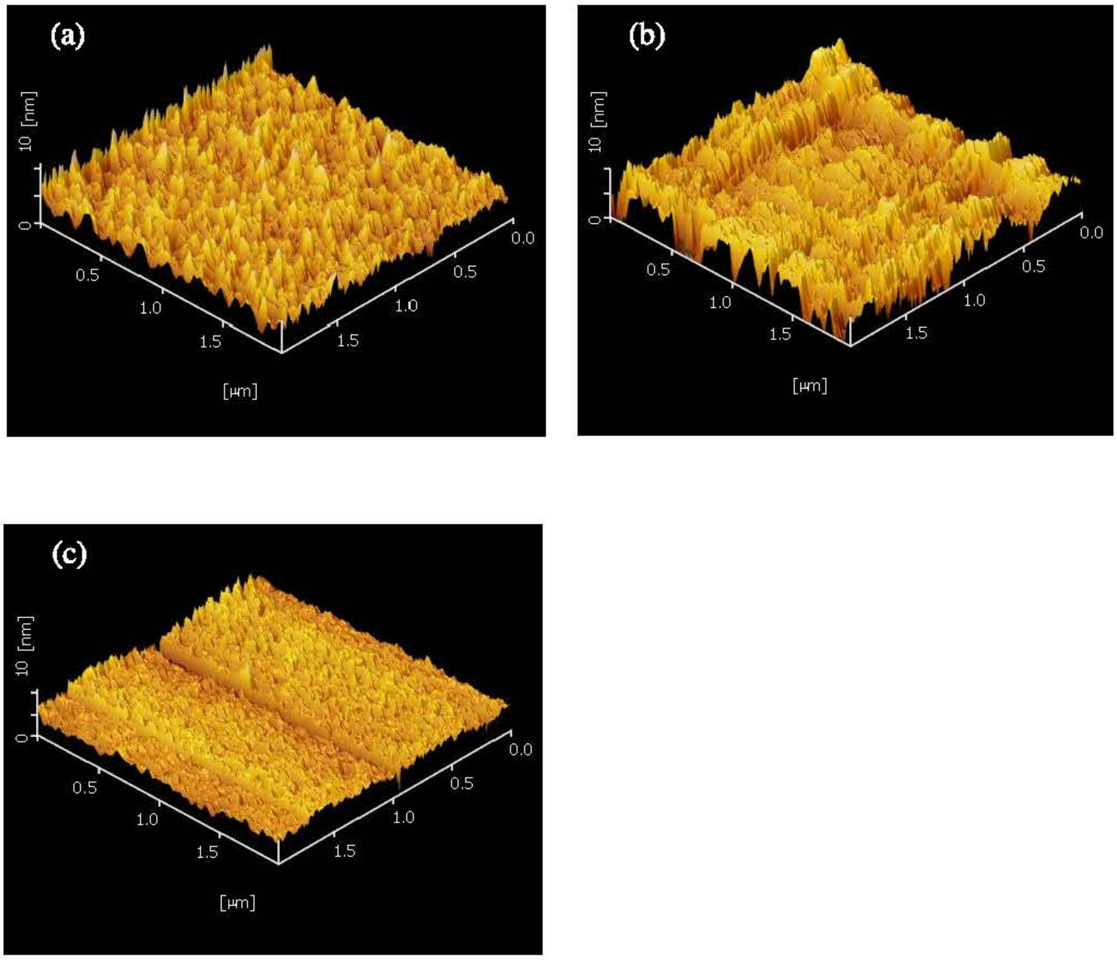

Figure 4.16 Surface nanotopography of PET films (a) non-treated, (b) corona treated 1, line speed 410 m/min, 9 KW, (c) corona treated 4, line speed 410 m/min, 6.7 KW.

Figure 4.17 shows the roughness of chemical treated films (b and c) are smoother than non-treated PET film (a), but got similar surface tension, shows in table 4.3. Due to the thin film of chemical coated to cover the surface of the film. Sometime the chemical treated PET film has inconsistency on roughness (a and b) which may be from improper preparation coating solution or unequal coating of chemicals, shows in figure 4.18. This problem not effect to normal application but will effected to some special application such as metallize process (aluminium coating by thickness 200-500 angstrom), the problem is aluminium peel off due to low bonding strength.

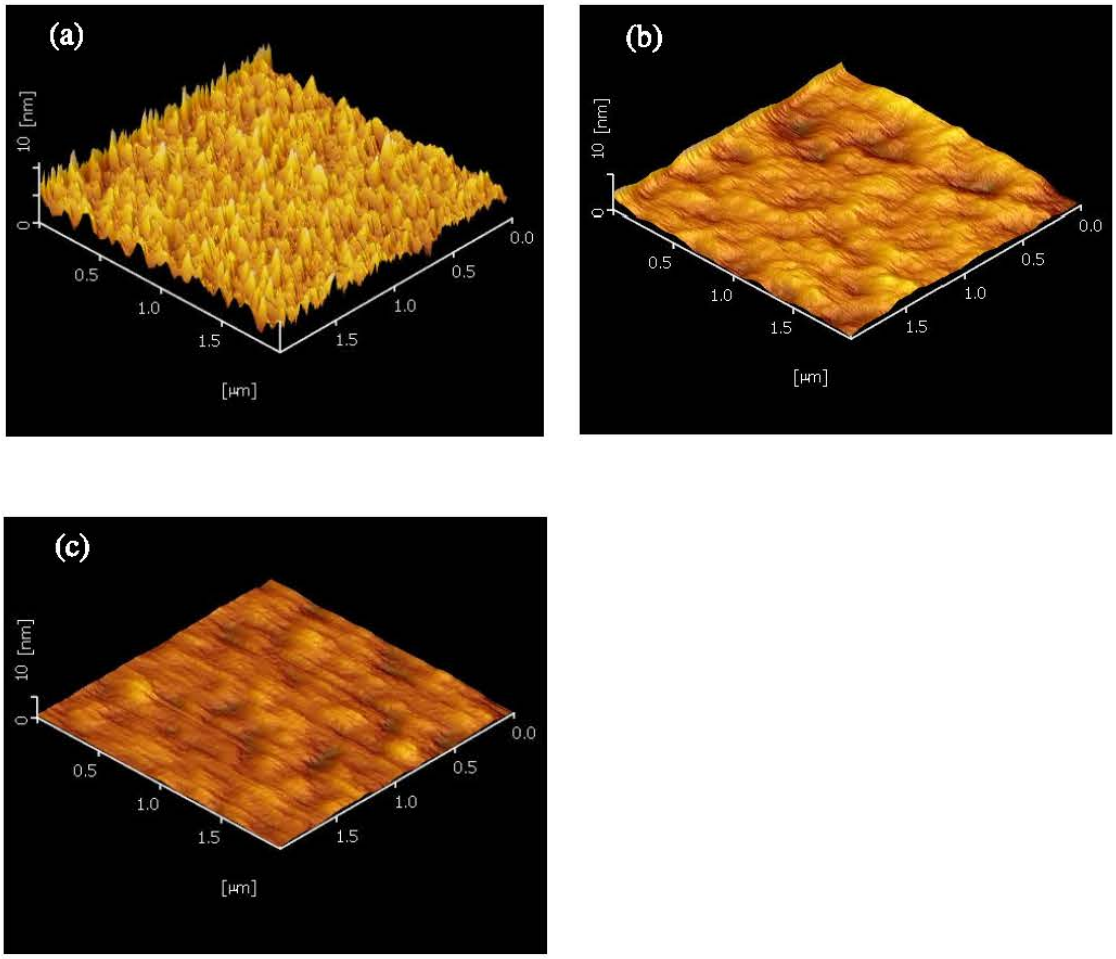

Figure 4.17 Surface nanotopography of PET films (a) non-treated, (b) chemical treated 1, line speed 390 m/min, (c) chemical treated 2, line speed 320 m/min.

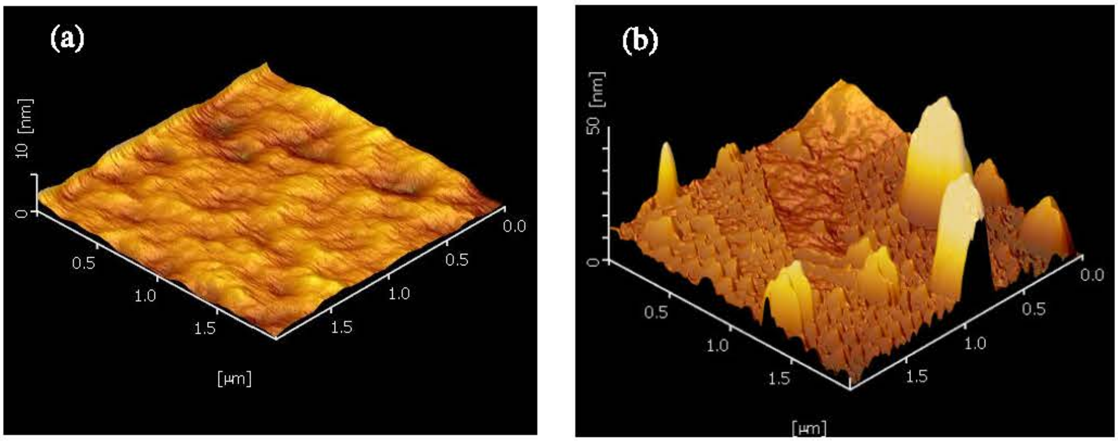

Figure 4.18 Surface nanotopography of PET films (a) chemical treated (good one), line speed 320 m/min, (b) chemical treated (bad one), line speed 320 m/min.

The comparison of surface roughness between plasma and corona treatments figure 4.19 shows that plasma treatment (b) makes smoother surface to corona treatment (c and d). Due to plasma treatment used low power treatment and higher production line speed, but got similar surface tension (dyne value 58-61), shows in table 4.3.

The comparison of surface roughness between plasma and non-treated films figure 4.19 shows that plasma treatment (b) makes nearly similar surface roughness to non- treated (a) but got higher surface tension (dyne value 58-61for plasma treated and 40-42 for non-treated), shows in table 4.3, due to main effect of plasma treatment to the chemical structures or functional groups but not too much effect to the surface roughness.

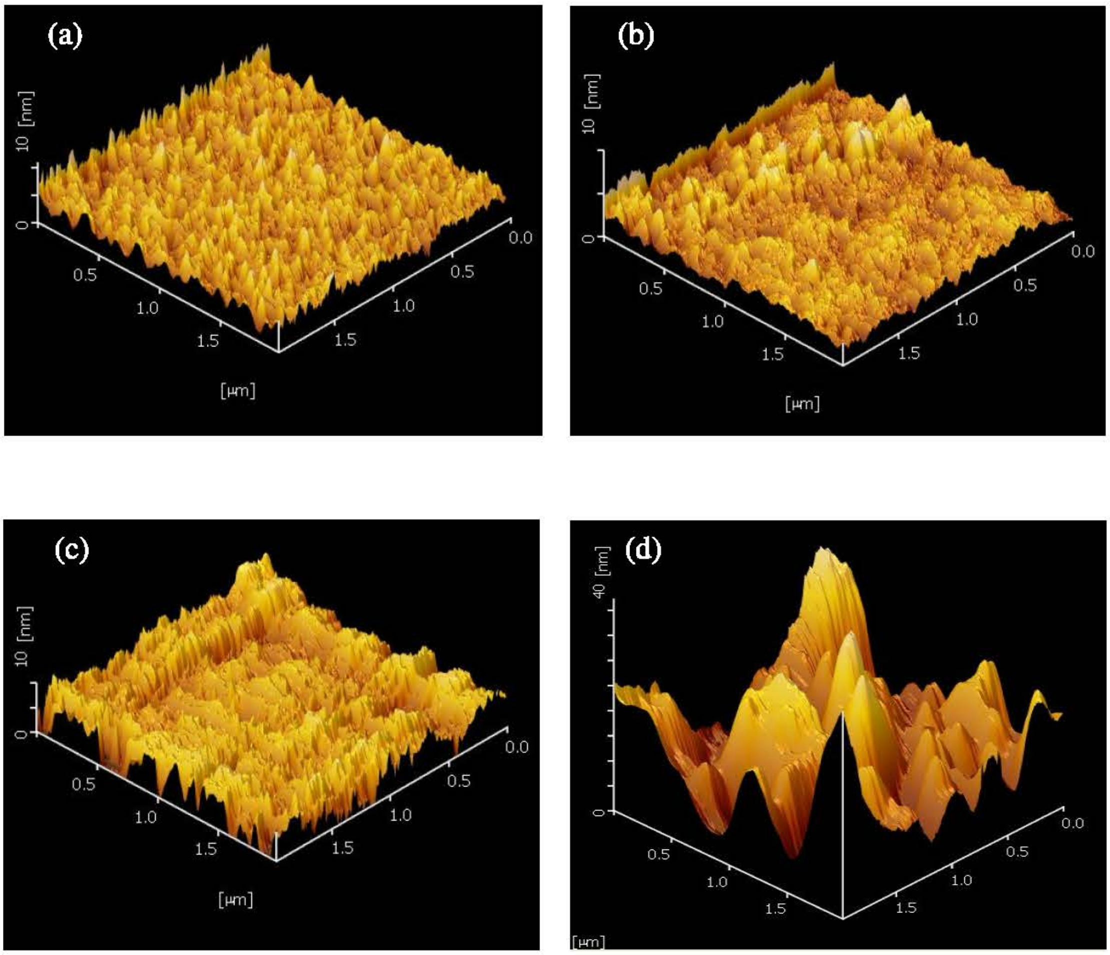

Figure 4.19 Surface nanotopography of PET films (a) non-treated, (b) plasma treated, line speed 600 m/min, 4 KW, (c) corona treated 1, line speed 410 m/min, 9 KW, (d) corona treated 2, line speed 210 m/min, 9 KW.

4.3. Surface tension

4.3.1 Dyne value

The extent of hydrophilicity of the surface modified PET films was investigated by dyne value measurement. Table.4.3 show the variation in the dyne values of the PET films for different treatment times and different modification techniques. As it can be observed, the dyne value of the non-treated surface is 40-42. The dyne values reached up to 58 – 61 after being treated by corona and plasma treatments. For chemical treatment, the dyne values reached up to 56 – 61. After kept the sample around 2 years at ambient temperature 30-40 °C found that dyne value of non-treated, corona treated and chemicals treated not changed but has changed for plasma treated film, the dyne value was dropped from 58-61 to be <40 and matched to the result of contact angle table 4.4 show the contact angle of plasma treated to similar to non-treated film. This may due to bonding of chemical functional groups from plasma treatment was broken and also the surface of plasma treated film is very smooth similar to non-treated film (dyne value 40-42).

Table 4.3 Surface tension of films after treatment.

	Non-treated	Chemical		Plasma	Corona			
		1	2	1	1	2	3	4
Production Line Speed (m/min)	420	390	320	600	410	210	150	410
KW	-	-	-	4	9	9	9	6.7
Dyne value Minimum	40	56	56	58	58	58	58	58
Dyne value Minimum After kept 2 years	40	56	56	-	58	58	58	58
Dyne value Maximum	42	61	61	61	61	61	61	61
Dyne value Maximum After kept 2 years	42	61	61	<40	61	61	61	61

4.3.2 Contact angle

The surface modified PET films after kept around 2 years at ambient temperature 30-40 °C was investigated by contact angle measurement. Table 4.4 shows the variation in the contact angle values of the PET films for different treatment times and different modification techniques. As it can be observed, the contact angle of the non-treated and plasma treated films are around 69-69.6. The contact angle of corona treated films are 60-65 and chemical treated films are around 65.5-66.5. The result are matching to dyne value table 4.3.

Table 4.4 Contact angle of films after treatment and kept 2 years.

	Contact angle (θ) avg.
Non-treated	69.6
Corona treated 1, line speed 410 m/min, 9 KW	62.3
Corona treated 2, line speed 210 m/min, 9 KW	59.8
Corona treated 3, line speed 150 m/min, 9 KW	64.8
Corona treated 4, line speed 410 m/min, 6.7 KW	61.3
Plasma treated, line speed 600 m/min, 4 KW	69.1
Chemical treated 1, line speed 390 m/min	65.7
Chemical treated 2, line speed 320 m/min	66.4

CHAPTER V

CONCLUSIONS AND RECOMMENDATION

5.1 Conclusion

Corona, plasma and chemical treatments improve the surface properties of PET films. Attenuated total reflectance-Fourier transform infrared spectroscopy (ATR FT-IR) and Raman spectroscopy can't analyze the changes of the chemical structures or functional groups such as C–O, O=C–O and C=O after modification due to the depth of modified surface not enough. The AFM observation showed the etching effect on the polymer surface. Contact angle and dyne value observation showed the variation of the surface tension.

The changing of chemical structures or functional groups is more important than nanotopographical changes because of the films with similar roughness (plasma treated and non-treated) or the smooth surface (chemical treated and non-treated) are able to reach the higher surface tension.

Plasma treated film can't keep for the long time after treated may from unstable of the bonding of chemical structure or functional group from treatment.

5.2 Recommendation

Due to this study have to used attenuated total reflectance-Fourier transform infrared spectroscopy (ATR FT-IR) and Raman spectroscopy but can't analyze the change of the chemical structure or functional group, recommended to use X-ray photoelectron spectroscopy (XPS) to analyze the changes of chemical structures or functional groups.

Due to etching effect of corona treatment on film surface, the production line speed should match electric corona power being applied to prevent the bulk mechanical properties changes and for energy saving.

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